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OPTICAL PROPERTIES OF ALKALI HALIDE AND THALLIUM HALIDE SINGLE CRYSTALS

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The large single crystals of alkali halide and thallium halide were produced by Bridgman-Stockbarger method. The absorption spectra of KRS-5, TlBr and TlCl with the several thickness near the short edge were measured and compared with the results of various investigators. Although the exciton peak was not detected, the impurity band of thallium compound and the red shift of short edge were found. Also, their reflectance spectra of NaF, TlCl and KRS-5 in the far infrared region were measured. And these results were analysed referring to the Drude's dispersion formula, thus the damping constants of these crystals at room temperature were estimated to be 0.045 for NaF, 0.15 for TlCl, and 0.18 for NaF respectively.

Introduction

In general, the methods for growth of crystals have been selected following the melting point, crystal structure and chemical properties of materials. The several methods have been devised for crystal growth of various materials[1~6], and in some cases the theories on the crystal growth[7] have been established. But the suitable technique for growing crystal of one material can not be simply applied for the similar one, thus many trials are often necessary before good crystals of given materials may be produced.

The author produced these crystals by Bridgman-Stockbarger method[1,2,6] by the reason that this method is most appropriate to clear the hysteresis of crystal growth. The most suitable conditions for growth to obtain nearly perfect crystal were found for each crystal, especially for the growth rate and the temperature distribution in the furnace.

It is found some difference in the separation of the first absorption band due to exciton creation from the one set of continuous absorption associated with band-to-band transition of alkali halide, where the nature of the bond is predominantly ionic, and of thallium halide with higher dielectric constant. In the later, the separation is less well resolved.

The exciton bands of these crystals have been measured by Pohl[8] and the others using thin

1) D. C. Stockbarger, *Rev. Sci. Instr.*, 7, 133 (1936)
2) D. C. Stockbarger, *Diss. Faraday Soc.*, No. 5, 294 (1949)
3) S. Kyropoulos, *Z. anorg. Chem.*, **154**, 308 (1929)
4) S. Kyropoulos, *Z. Physik*, **63**, 849 (1930)
5) F. Stober, *Z. Krist.*, **61**, 299 (1925).
6) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **60**, 303 (1925)
7) H. E. Buckley, *Crystal Growth*, John Wiley and Sons, Inc., New York (1951), p. 169
8) R. Hilsch and R. Pohl, *Z. Physik*, 59, 812 (1930)

evaporated film of these crystals.[9,10,11] The optical properties of evaporated thin film and of the thin film of single crystal probably may be different for the reason that the evaporated thin film is the aggregation of very small particle. To detect the exciton bands of thallium halide single crystals, the author polished the specimens of TlCl, TlBr and KRS–5 as thin as possible, and measured the absorption spectra near the short edge.

On the other hand, many investigators[12)13)] have discussed from the knowledge of the optical constant about the reflection structure, especially about their side bands and the broadening of their main bands. The dependances of the damping constants of NaCl and LiF lattice vibration on the temperature were estimated by Hass[14)] and Heilmann[15)].

To estimate of the damping constants in lattice vibration of the single crystals of NaF, TlCl and KRS–5, using the Drude's dispersion formula[16)], the reflection spectra of these crystals in the far infrared region were measured.

Experimentals

The raw materials used to produce the single crystals of alkali halides and thallium halides were available the commerciallized reagents with the highest purity. The reagents were purified by the zone refining method and the cationic impurities in the starting materials are partially listed in the table, determining by flame analysis. In the table, the notations of $+$, $\pm$ and $-$ represent that the impurity contents are $10^{-4}\sim10^{-5}$, $10^{-5}\sim10^{-6}$ and below 10^{-6} in weight respectively.

Table The impurity contents in the raw materials.

Impurity / Crystal	Ca	Al	Pb	Fe	Ag	Ti	Cu	Mg	Si
TlCl	+	+	+	+	+	±	+	+	+
TlBr	+	+	+	+	±	−	+	±	−
KRS–5	+	+	+	+	±	−	+	±	−

These raw materials of KRS–5 (mixed crystal of 42 atom per cent TlBr and 58 atom per cent TlI), TlBr and TlCl were sealed in glass tubes with the crucible made of platinum or porcelain, which took the shape of cone in the lower part and cylinder in the upper part. Before sealing these materials were dried for about fifty hours long at high temperature below the hydrolysis temperature to avoid the reaction with water under crystalization. For NaF, the same

9) E. G. Schneider and H. M. O. Bryar, *Phys. Rev.*, **51**, 293 (1937)
10) H. Fesefeldt, *Z. Physik*, **64**, 623 (1930)
11) W. Martienssen, *J. Phys. Chem. Solids*, **2**, 257 (1957)
12) L. Genzel, H. Happ and R. Weber, *Z. Physik.*, **154**. 13 (1959)
13) A. Mitsuishi, H. Yoshinaga, and S. Fujita, *J. Phys. Soc. Japan*, 14, 110 (1959)
14) M. Hass, *Phys. Rev.*, **117**, 1497 (1960)
15) G. Heilmann, *Z. Physik*, **154**, 13 (1959)
16) M. Born and K. Haung, *Dynamical Theory of Crystal Lattice*, Oxford Univ. Press, New York (1954), p. 121

The Review of Physical Chemistry of Japan Vol. 30 No. 1 (1960)

treatment was applied without sealing. The schematic diagram of the furnace using Bridgman-Stockbarger method to produce the single crystals is shown in Fig. 1. An example of optimum

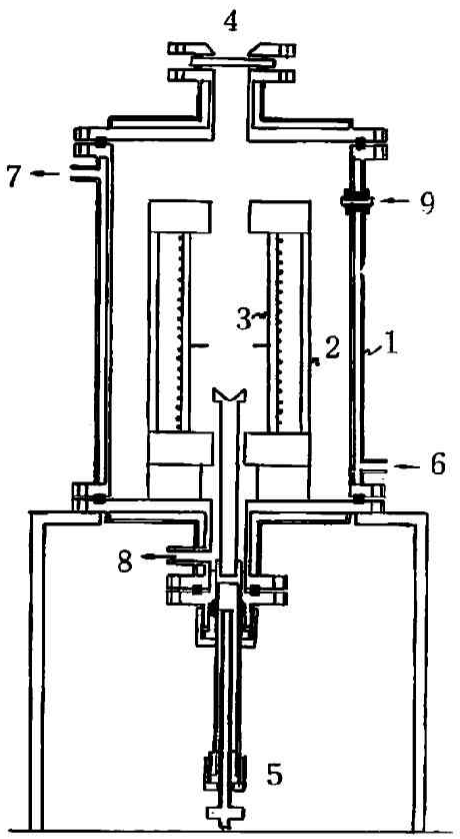

Fig. 1 The schematic diragram of the furnace employed for crystal growth

1: steel pipe of water jacket
2: radiation baffle
3: heater
4: window
5: lowering controller
6: water inlet
7: water outlet
8: to vacuum pump
9: power connection

conditions of the temperature distributions which were changed with crystalization process is shown in Fig. 2. It was necessary to give the largest temperature gradient in the solid-liquid phase in the crucible as possible for the generation of only a single nuclear crystal. After the crystal was partially grown, it was necessary the temperature gradient to be mollified and the isothermal line to be vertical to the direction of growth. In the final process, it was necessary the temperature gradient to be mostly mollified.

The lowering rates of crucible which have the optimum conditions depending on the kinds of crystals were ranged from 1mm/hr to 6mm/hr. And the lowering rate of crucible can be regarded as the crystal growth rate, by controlling the temperature gradient in the furnace with the appropriate design. This was ascertained by the intermittent observation. The transparent single crystals of the alkali halides and thallium halides have been produced with these procedures. The ingots were cut in appropriate size to measure their optical properties and polished on the pitch plate using zirconium oxide powder. As shown in Fig. 3, the optical absorption spectra near the short edge were measured with the spectrometer, the Model Hitachi EPU-2A,

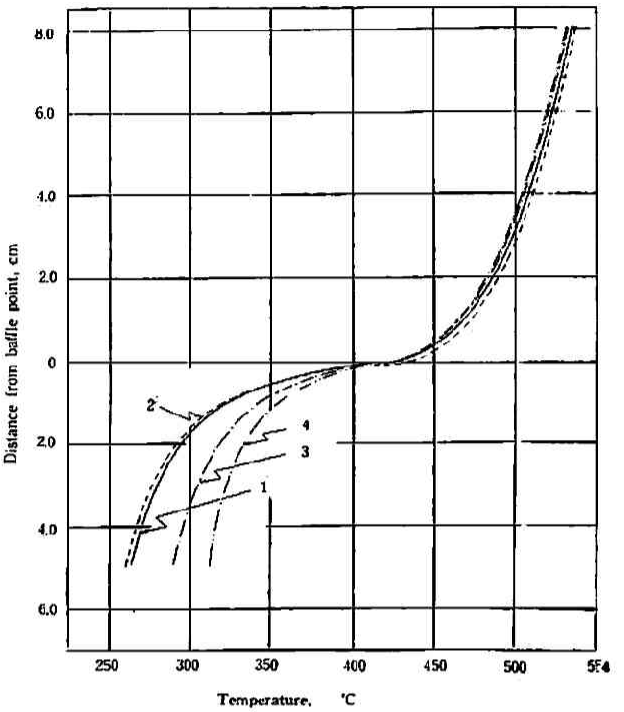

Fig. 2 The optimum temperature distribution curves of the furnace for crystal growth
1: at center of furnace, beginning of growth
2: at exterior of furnace
3: at center of furnace, half of growth
4: at center of furnace, final of growth

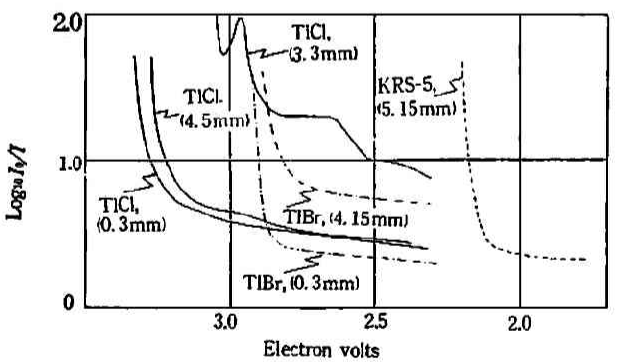

Fig. 3 The absorption spectra near the short edge of TlCl, TlBr and KRS-5 with the various thickness

in terms of the quantity, $\log(I_0/I)$, where I_0 is the intensity of the incident beam and I is the intensity of the light transmitted by the sample. All measurements were operated at room temperature.

On the other hand, as shown in Fig. 4, the reflection spectra of NaF, TlCl and KRS-5 crystal in the far infrared region with the vacuum grating spectrometer of much higher resolving power, were measured at Yoshinaga Laboratory, Faculty of Technology, Osaka University. The measurements were made in the spectral region from 20 μ to 200 μ, at the average incident angle 12° at room temperature.

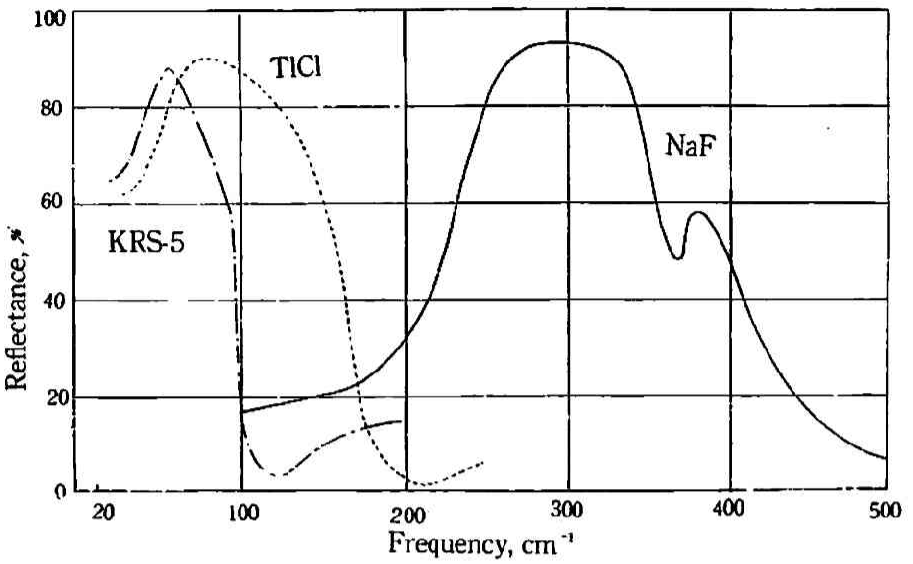

Fig. 4 The reflection spectra of NaF, TlCl and KRS-5 in the far infrared region at the incident angle 12°

Results and Discussions

In Fig. 3 are given the absorption spectra near absorption edges of TlCl, TlBr and KRS-5 single crystals. The specimens were too thick to detect the exciton band as shown in Fig. 3. The edges are sited at 3.35 ev for TlCl, 2.94 ev for TlBr and 2.21 ev for KRS-5, and are shifted to the longer wavelength side than those of other results, in which are at about 4.5 ev for TlCl, at about 4.2 ev for TlBr[17] and 2.29 ev for KRS-5[18] respectively. Contamination of thallium compound as impurity to thallium chloride results in the impurity band at 3.15 μ, in absorption spectra and more shift to longer wavelength side of the absorption edge compared with pure TlCl. The chemical formula of the thallium compound impurity may be thallium oxide. This was ascertained by the chemical analysis of the impurity rich portion of TlCl. In Fig. 4 are shown the infrared reflection spectra of NaF, TlCl and KRS-5.

The reflection spectra of crystals are expressed in the following manner using Drude's dispersion formula,

$$\epsilon(\omega) = \epsilon_0 + \frac{\epsilon_0 - \epsilon_\infty}{1 - \left(\frac{\omega}{\omega_0}\right) + i\left(\frac{\gamma}{\omega_0}\right)\left(\frac{\omega}{\omega_0}\right)}. \qquad (1)$$

The constants are directly measurable quantities, ω_0, ϵ_0 and ϵ_∞ represents the infrared dispersion frequency, the static dielectric constant and the high-frequency dielectric constant respec-

17) S. Tutihasi, *J. Phys. Chem. Solids*, **12**, 344 (1960)

18) G. Toos, *Optical Properties of Solid*, F. I. A. T. *Review of German Science* 1936–1946 Part II; *The Physics of Solid* (P. B. 95684)

tively.

And the damping term was expressed as (γ/ω_0). $\varepsilon(\omega)$ defines a complex dielectric constant

$$\sqrt{\varepsilon(\omega)} = n - i\kappa, \tag{2}$$

where n is the index of refraction and κ is extinction coefficient. By expressing Eq. (1) in terms of its real and imaginary parts, it is shown that

$$n^2 - \kappa^2 = \varepsilon_\infty + \frac{(\varepsilon_0 - \varepsilon_\infty)[1 - (\omega/\omega_0)^2]}{[1 - (\omega/\omega_0)^2]^2 + (\omega/\omega_0)^2(\gamma/\omega_0)^2}, \tag{3}$$

$$2n\kappa = \frac{(\varepsilon_0 - \varepsilon_\infty)(\gamma/\omega_0)(\omega/\omega_0)}{[1 - (\omega/\omega_0)^2]^2 + (\omega/\omega_0)^2(\gamma/\omega_0)^2}, \tag{4}$$

Knowing n and κ, the reflectance R is given by

$$R = \frac{(n-1)^2 + \kappa^2}{(n+1)^2 + \kappa^2}. \tag{5}$$

The results of calculating R as function of (ω/ω_0) are shown in Figs. 5, 6 and 7. The determination of the value of ε_0 and ε_∞ were taken as 6.0 and 1.74 for NaF, 32.5 and 5.99 for KRS–5, and 31.9 and 2.25 for TlCl[19].

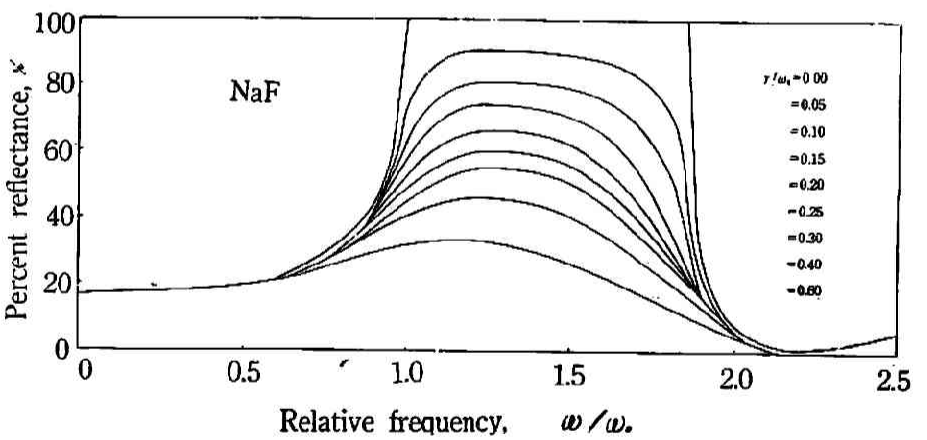

Fig. 5 The reflection spectra calculated from the dispersion formula with the damping constant as a function of the relative frequency in NaF

The inverse curves of the peak reflectivity were then plotted as a function of the damping constants as shown in Figs. 8, 9 and 10. It can be seen from these Figures that the inverses of peak reflectivity are approximately linear with the damping constant as has been shown in the other paper. Consequently, the damping constant can be estimated to be 0.045, 0.15, and 0.18 for NaF, TlCl, and KRS–5 respectively at room temperature.

Lax and Burstein[20] showed that the relative width of the main peak decreases in order

19) K. Hiendahl, *K. Danske Vidensk, Selskab.*, **16**, No. 2 138 (1955)
20) M. Lax and E. Burstein, *Phys. Rev.*, **97**, 39 (1955)

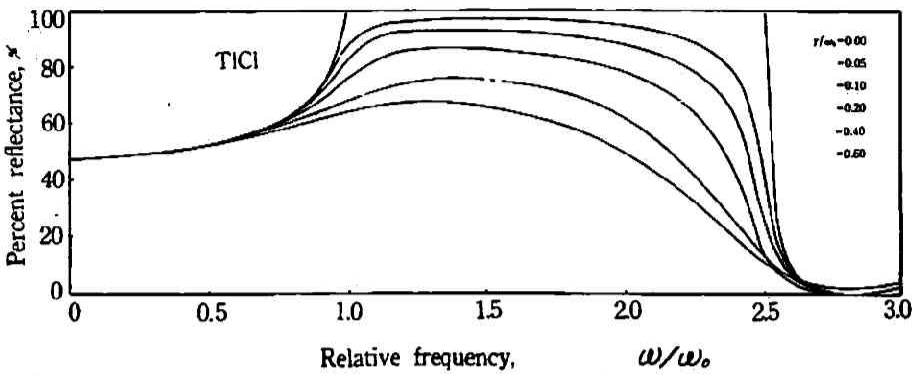

Fig. 6 The reflection spectra calculated from the dispersion formula with the damping constant as a function of the relative frequency in TlCl

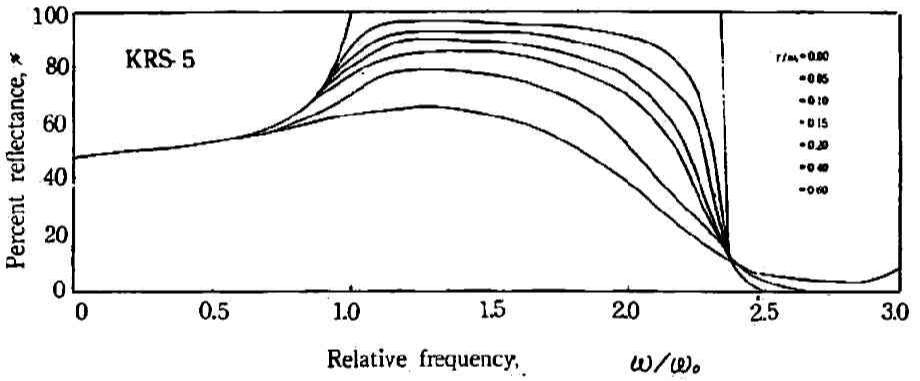

Fig. 7 The reflection spectra calculated from the dispersion formula with the damping constant as a function of the relative frequency in KRS-5

LiF, NaF, NaCl and KCl and that the relative heights of the secondary side peak to major one also decrease in exactly the same order. A similar trend is found in these crystals for the deviation from the Caucy relation among the elastic constants C_{44}/C_{12} in these crystals. By the analysis of reflection spectrum following the harmonic approximation when cyclic boundary conditions are employed, the occurrence of a complex spectrum can not be explained. The existence of the side band in the reflection spectrum of NaF indicates the inadequacy of the simple theory, as pointed out by Hass. But the main bands in the reflection spectrum estimated, shown in Figs. 5, 6 and 7, show the good agreement with those of the experimental results shown in Fig. 4, when the damping constants of NaF, TlCl and KRS-5 are decided to be 0.045, 0.15 and 0.18 respectively.

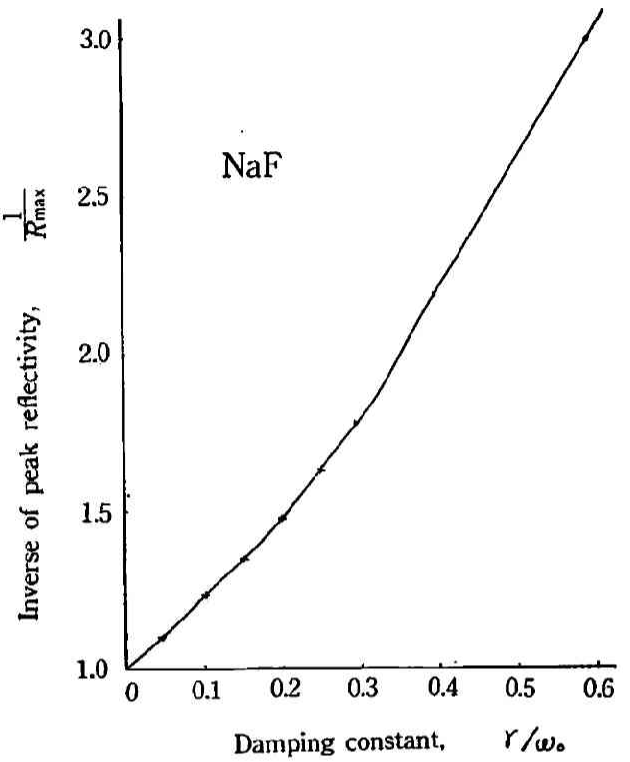

Fig. 8 The inverse of peak reflectivity as a function of the damping constant in NaF

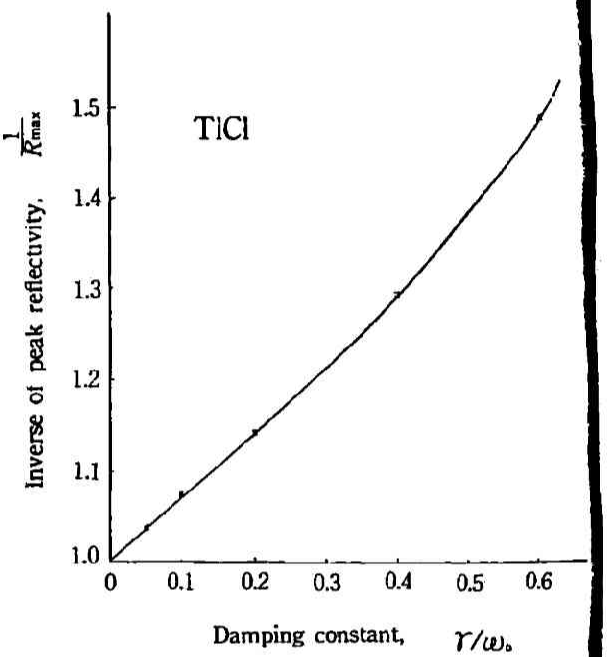

Fig. 9 The inverse of peak reflectivity as a function of the damping constant in TlCl

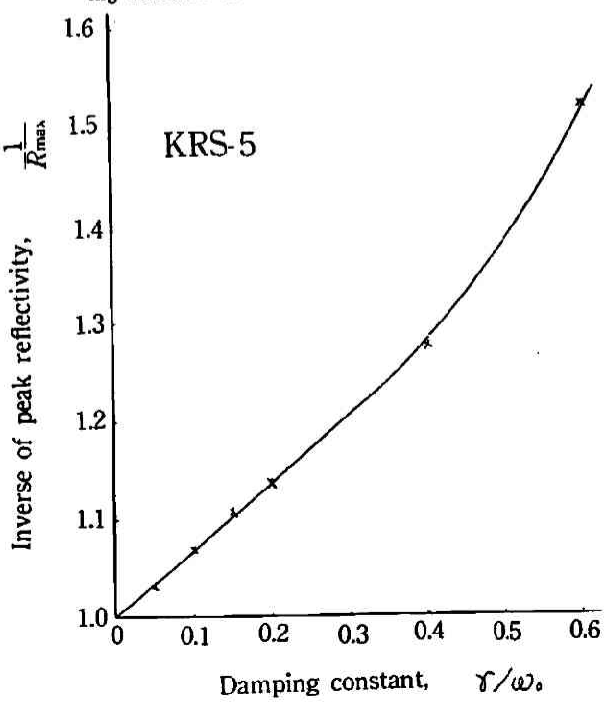

Fig. 10 The inverse of peak reflectivity as a function of the damping constant in KRS-5

The Review of Physical Chemistry of Japan Vol. 30 No. 1 (1960)

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